

CLEAN VERSION OF PARAGRAPHS INCORPORATING CHANGES MADE

Please replace the paragraphs in page 1, line 5 – page 2, line 2 with the following:

The present invention relates to a lithium secondary battery in which the deterioration of battery properties attributed to water released from both a positive electrode and a negative electrode and existing in the non-aqueous electrolytic solution packed in the battery is suppressed.

(2) Description of Related Art

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A lithium secondary battery, in recent years, has widely been employed as a secondary battery chargeable and dischargeable, small in size, having a high energy density, and capable of functioning as an electric power source of electronic appliances such as portable communication appliances, notebook type personal computers and the like. Further, in the situation where people have been paying much attention to resource saving and energy saving for the international protection of global environments, the lithium secondary battery is expected to be used, in the automobile industry, as a battery for driving a motor of an electric automobile and a hybrid electric automobile and, in the electric power industry, as a means for efficiently utilizing electric power by storing night time electric power. It is, therefore, urgently required to develop a lithium secondary battery with a large capacity which is practically suitable for the above applications.

Please replace the paragraph in page 3, line 22 – page 4, line 7 with the following:

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For example, as will be mentioned later, using an organic binder, an electrode active material is applied to a current collector substrate and formed into a prescribed shape such as a tape-like shape and during the forming process, the electrode active material is mixed with an organic solvent or water to be in the

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slurry or paste state to be used. At the time of producing a slurry, in the case where an insufficiently dried raw material of an electrode active material is used or the water concentration of the organic solvent used for the slurry production is not controlled and subsequently, the water control in the produced slurry is imperfect, the probability of adsorption of water in the electrode active material is extremely high.

Please replace the paragraph in page 5, lines 3 - 12 with the following:

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Inventors of the present invention have sincerely studied to deal with the above-described problems in the conventional technique and subsequently found that excellent charging and discharging efficiency and cycle property can be obtained in the case where water released from both a positive electrode and a negative electrode after both electrode plates are packed in a battery and consequently existing in a non-aqueous electrolytic solution is at a prescribed value or lower and thus developed the present invention.

Please replace the paragraph in page 6, lines 1 - 17 with the following:

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The lithium compound to be used preferably for such a lithium secondary battery of the present invention is lithium hexafluorophosphate. Further, a material to be employed for the electrode active material is not specifically limited and in the case where lithium manganese oxide containing lithium and manganese as main components and having a cubic system spinel structure is used as the electrode active material, the internal resistance of the battery can be suppressed. Furthermore, a highly graphitized carbon fiber is preferably used as the negative

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electrode active substance. The present invention is suitably applied to a large scale battery having a battery capacity of 2 Ah or more. Also, a lithium secondary battery of the present invention is suitably used as an electric power source for driving a motor of an electric automobile or a hybrid electric automobile in which large current discharge is frequently caused.

Please replace the paragraph in page 7, lines 11 – 17 with the following:

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One structure of an electrode unit, which may be compared to a heart part, of a lithium secondary battery is a single cell structure comprising a positive electrode active substance and a negative electrode active substance press-molded into a disk-like shape with a separator interposed between them, such a structure being of a coin type battery with a small capacity.

Please replace the paragraphs in page 8, line 6 – page 9, line 6 with the following:

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Another structure of the electrode unit includes a laminated type obtained by laminating a plurality of electrode units each applicable for a single cell type coin battery. As shown in Fig. 2, a laminated type electrode unit 7 is obtained by reciprocally laminating positive electrodes 8 and negative electrodes 9 both with prescribed shapes while interposing separators 10 between them and connecting at least one electrode lead 11, 12 respectively to each one of electrodes 8, 9. The materials used for the electrodes 8, 9, the production methods therefor, and the like are the same as those of the electrodes 2, 3 in the rolled type electrode unit 1.

Next, using the wound type electrode unit 1 as an example, the constitution will be described in detail. The positive electrode 2 is produced by applying a

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positive electrode active substance to both sides of a current collector substrate. A metal foil such as an aluminum foil, a titanium foil, and the like excellent in corrosion resistance to cathodic electrochemical reactions is preferably used for the current collector substrate and further besides the foil, a punched metal or a mesh may also be employed. Preferable compounds to be used for the positive electrode active substance are lithium transition metal compound oxides such as lithium manganese oxide (LiMn_2O_4), lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), and the like and it is preferable to add, as a conductivity-improving agent, a fine carbon powder such as acetylene black or the like to these compounds.

Please replace the paragraph in Page 9, lines 20 – 27 with the following:

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In this case, the substituent element M is an element forming a solid-solution in the LiMn_2O_4 theoretically in the form of monovalent Li; bivalent Fe, Mn, Ni, Mg or Zn; trivalent B, Al, Co, or Cr; tetravalent Si, Ti, and Sn, pentavalent P, V, Sb, Nb, or Ta; or hexavalent Mo or W cation. The following are also possible: Co and Sn are bivalent; Fe, Sb, and Ti trivalent; Mn trivalent or tetravalent; and Cr tetravalent or hexavalent.

Please replace the paragraphs in page 10, line 14 – page 12, line 14 with the following:

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The negative electrode 3 can be produced in the same manner as for the positive electrode 2. A metal foil such as a copper foil, a nickel foil, and the like excellent in corrosion resistance to anodic electrochemical reactions is preferably used for the current collector substrate of the negative electrode 3. The compounds

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to be used for the negative electrode active substance are amorphous carbonaceous material powder such as soft carbon and hard carbon, highly graphitized carbonaceous material powder such as synthetic graphite and natural graphite.

As the separator 4, it is preferable to use a three-layer structure comprising a microporous and Li^+ -permeable polyethylene film (PE film) and porous and Li^+ -permeable polypropylene films (PP films) sandwiching the PE film between them. In the separator, when the temperature of the electrode unit is increased, the PE film is softened at about 130°C and the micropores are broken and thus the separator functions also as a safety mechanism of suppressing the movement of Li^+ , i.e. the battery reactions. By sandwiching the PE film between PP films of a higher softening point, the PP films retain the shape to prevent contact and short circuit between the positive electrode 2 and the negative electrode 3, to reliably suppress the battery reactions, and to secure the safety even when the PE film is softened.

During the winding work of the electrode plates 2, 3 and the separator 4, electrode leads 5, 6 are separately joined to a part of each of the electrodes 2, 3 in which no electrode active substance is applied and where each current collector substrate is exposed. As the electrode leads 5, 6, it is preferable to use those made of foils of the same materials as those of the current collector substrates of the respective electrodes 2, 3. The joining of the electrode leads 5, 6 to the electrodes 2, 3 can be carried out by ultrasonic welding, spot welding or the like. In that case, as shown in Fig. 1, it is preferable to join electrode leads 5, 6 in a manner where one of the electrode leads of the respective electrodes is joined to one end face of the electrode unit 1, for the electrode leads 5, 6 can be kept from contact with each other.

In the case of assembling a battery, at first, the produced electrode unit 1 is inserted into a battery case and held in a stable position while the electric

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communication of terminals for taking electric current out to the outside with electrode leads 5, 6 is reliably secured. After that, the electrode unit is impregnated with a non-aqueous electrolytic solution and then the battery case is sealed to produce a battery.

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Next, the non-aqueous electrolytic solution to be employed for a lithium secondary battery of the present invention will be described. Preferable examples of the solvent are carbonic acid esters such as ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC), and the like; single solvents such as γ -butyrolactone, tetrahydrofuran, acetonitrile, and the like; and their mixtures.

Please replace the paragraph in page 13, lines 11-20 with the following:

In a battery produced in such a manner, although water released from the electrode plates inevitably exists in the non-aqueous electrolytic solution, the precise amount of the water and the effect of the water on the battery properties have not been made clear. The inventors of the present invention, therefore, have precisely detected the amount of water existing in the electrode plates and subsequently contained in the electrolytic solution and found the relation between the water amount and the deterioration of the battery properties and developed the present invention.

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Please replace the paragraphs in page 15, line 22 – page 17, line 15 with the following:

As described above, the increase of the temperature of the electrode plates means the observation of the water release from the electrode plates with the lapse of time and can correspondingly be considered as alteration of the battery properties with the lapse of time. In other words, that the temperature is increased owing to heating of the electrode plates at 25 to 200°C and at 200 to 300°C can be supposed to be causes of deterioration of battery properties for the middle and long periods from immediately after production of the battery.

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Consequently, by producing electrodes in which the water concentration is regulated to the forgoing prescribed values or lower in the respective temperature ranges, a battery showing excellent battery properties immediately after battery production and in a long duration can be produced. Further, in the case where only a single property, i.e. the high initial charging and discharging efficiency, the excellent self-discharging efficiency, or the cycle property, is required respectively, for example, in the case where a battery has a relatively short utilization period and a long cycle property is not required, it is sufficient for the electrode plates to satisfy the prescribed water concentration at 25 to 200°C and it is not required to take the water concentration at 200 to 300°C into consideration for the electrodes. That is, if a battery is required to have separate properties, the electrodes may be produced in consideration of the required properties alone.

Meanwhile, the Karl Fischer method is preferably employed for the measurement of the concentration of water released from both of the positive electrode and the negative electrode. At the time of actual measurement, as shown in Fig. 3, the measurement is carried out by putting both electrodes to be subjected

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to the measurement in an electric furnace 15 through a specimen setting inlet 16, increasing the temperature of the electrodes by a heating pipe 17 in the inert gas flow, and sending the released water to a measurement part 20 through a suction pipe 21.

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In the Karl Fischer method, a non-aqueous electrolytic solution is dissolved or dispersed in methanol and the resulting sample solution is titrated with a reddish brown Karl Fischer reagent, a reagent for water quantitative determination for the volumetric analysis, obtained by dissolving iodine, sulfur dioxide, and pyridine in methanol ordinarily at a molecular ratio of 1 : 3 : 10 and the measurement can be carried out by observing the alteration of the color of the reaction solution by a colorimetric titration, a potentiometric titration, or an amperometric titration.

Please replace the paragraph in page 18, lines 9 – 26 with the following:

Table 1 shows the results of evaluation of the initial charging and discharging efficiency, the self-discharging efficiency, and the cycle property of each of the foregoing examples. The electrodes of respective examples 1 to 5 were produced by the above described method using various electrode constituent members which were so adjusted as to cause the difference in the concentrations of water released from the respective electrodes. The other members and the testing environments were the same for all of the samples and the battery members were sufficiently dried immediately before the assembly of the respective batteries and there is eliminated the effect of water penetration from the outside of the batteries due to defective sealing of the batteries. In addition, a solution containing a mixed solvent of EC and DEC in the same volume and LiPF₆ as an electrolyte dissolved in

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the mixed solvent in 1 mol/l concentration was employed as a non-aqueous electrolytic solution.

Please replace the paragraphs in page 21, line 15 – page 22, line 12 with the following:

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As understood from Table 1, if the cumulative concentration of water released from both a positive electrode and a negative electrode in relation to the weight of an electrode unit besides the current collectors was suppressed to 5,000 ppm or lower in the case where both electrodes were heated at 25 to 200°C, it was found that the initial charging and discharging efficiency was kept high. Also if the concentration was suppressed to 1,500 ppm or lower in the case where the electrodes were heated at 200 to 300°C, it was found that the self-discharging efficiency and cycle property were kept preferably. Subsequently, in the case of electrode plates satisfying the above described two conditions, batteries were found being provided with battery properties excellent in both the initial charging and discharging efficiency, and the self-discharging efficiency and the cycle property.

In the above, the present invention has been described mainly on a case using a wound type electrode unit. However, the present invention is applicable independently of the structure of a battery and can be employed suitably for a battery with a large capacity in which water control is not easy during the production process. More specifically, the capacity of the present invention can suitably be employed for a battery having a capacity of 2 Ah or more and comprising wound type or laminated type electrode units 1, 7.

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Please replace the paragraph in page 22, lines 20 – 27 with the following:

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According to the present invention, restriction is posed in the cumulative concentration of water released from both a positive electrode and a negative electrode and existing in the non-aqueous electrolytic solution packed in a battery. Consequently, the present invention is effective to improve the initial charging and discharging efficiency, the self-discharging efficiency, and the cycle property and to prolong the life of the battery.